

## **EXHIBIT D**

## **Polyurethane adhesives and binders**

By: Dr Berend Eling and Dr Chris Phanopolous,

Huntsman-Polyurethanes, Everslaan 45, 3078 Kortenbergh, Belgium

Polyurethane chemistry has added valuable contributions to the adhesive bonding technology making available many varied raw materials for the production of adhesives with a wide range of performance characteristics. Polyurethane adhesives vary widely in composition and are used in many different applications in various market segments.

Polyurethane adhesives are normally defined as those adhesives that contain a number of urethane groups in the molecular backbone or are formed during use, regardless of the chemical composition of the rest of the chain. Thus a typical urethane adhesive may contain, in addition to urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea and allophanate groups.

An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkage. Isocyanates will react with water to form a urea linkage and carbondioxide as a by-product. Linear thermoplastic PU's may be obtained by using compounds with two reactive groups such as diisocyanate and diols. When polyols with three or more hydroxyl groups (i.e. a functionality of 3 or more) are reacted with an isocyanate, or when isocyanates with three or more isocyanate groups are reacted with a polyol the resulting polymer is crosslinked. The amount of crosslinking affects the stiffness of the polymer. Contrary to linear polymers, crosslinked polymers will not flow when heated. All structural adhesives are crosslinked because this eliminates creep (deformation under constant load). In reaction systems where there is an excess of isocyanate crosslinking reactions may occur. These reactions form linkages of allophanate and biuret.

Urethane adhesives make good adhesives for a number of reasons:

- They effectively wet the surface of most substrates.
- They can interact with the substrate through polar interactions (e.g. hydrogen bonding).
- Their relatively low molecular weight/ small molecular size allows them to permeate porous substrates (for reactive adhesives).
- They can form covalent bonds with substrates that have active hydrogen atoms (for reactive adhesives).
- Through molecular composition the adhesive stiffness, elasticity and crosslinking can be tailored to suit specific needs.

The most commonly used isocyanates in polyurethane adhesives are MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate), both aromatic isocyanates. Aliphatic isocyanates are also used but in smaller volumes. Polyols of widely different types are used for the production of adhesives. The most commonly used polyols are polyether (polypropylene glycol) and polyester (adipate based) polyols.

Polyurethane adhesives can be classified in the following product segments:

Non-reactive Polyurethane adhesives:

1. Solvent borne adhesives. Polyurethane solvent adhesives consist of a high molecular weight hydroxyl terminated polyurethane (MW approximately 100,000) dissolved in a solvent. The polyurethanes are obtained by reacting a high molecular weight polyester diol with a diisocyanate and differ in solution viscosity and crystallisation tendency. The polymer solutions are applied to both surfaces to be bonded. Some time is allowed for the solvents to evaporate and the surfaces are then pressed together, at which point interdiffusion of the polymer chains will occur.
2. Hot melt adhesives. These adhesives also consist of high molecular weight hydroxyl-terminated polyurethane. Chemically and structurally the polymers used in solvent borne and hot melt adhesives are related. Hot melt adhesives are most commonly applied as adhesive film in lamination type of applications. These adhesives form the adhesive bond by cooling from the molten state.
3. Water based adhesives. These adhesives are high molecular weight polyurethanes dispersed in water (PU dispersions, or PUD's). The water carrier is eliminated during use, leaving the precipitated and coalesced polymer to form the adhesive bond.

#### Reactive Polyurethane adhesives:

1. One component adhesives. This is a liquid isocyanate-terminated polyurethane with a relatively high molecular weight (prepolymer) and rather low remaining isocyanate content. The prepolymers are prepared by reacting an excess of isocyanate with high molecular weight polyester or polyether polyols. The free isocyanate groups react with moisture from the environment to form urea linkages. If the functionality of the prepolymer is larger than two (i.e. contains more than two isocyanate groups per molecule) the cured film will be chemically crosslinked.
2. Two component adhesives. Such adhesives consist of two relatively low molecular weight components: the polyol and isocyanate. When the two components are mixed they form urethane groups in the adhesive films. The polyols are usually of the ether or ester type. The isocyanates and polyols employed may have a functionality of two or higher. In the latter case a crosslinked polymer film is formed.
3. Reactive Hot Melt. Reactive hot melt adhesives are highly viscous or solid prepolymers with a low melting point. The prepolymers are produced from solid (i.e. crystalline) polyester polyols and isocyanate and have a low number of free isocyanate groups. The adhesive is applied above its melting point and bond through the physical process of cooling (like a conventional hot melt adhesive) as well as through reaction with ambient moisture (as a one component adhesive).
4. Woodbinders: Aromatic isocyanates (predominantly MDI) are used as binders to manufacture oriented strand board (OSB), medium density fibreboard (MDF) and particleboard. For these boards, the isocyanate is blended with wood strands, fibres and chips, respectively. The cure takes place in a press at about 200°C. The

curing reaction is predominately via the reaction with water and thus the formation of urea groups. Additionally, a wide range of reactions with wood components will also occur depending on the temperature, moisture content and the specific location within the wood matrix.

5. Crosslinkers. Although crosslinkers are not seen as 'adhesives' perse, they do improve the adhesive properties of solvent and water born adhesives. Solvent borne crosslinkers are added to solvent born polyurethane or chloroprene adhesives. Water borne 'emulsifiable' isocyanates are added to latex and PUD adhesives. In the bond crosslinking reactions occur and the resulting crosslinked adhesive has improved mechanical properties as compared to the non-crosslinked adhesives.

#### Market segments:

Based on their outstanding properties, their simple and economical processing and their high strength, polyurethane adhesives have found broad use in many application areas. The segments in which polyurethane adhesives are used most are: footwear industry, construction, woodworking, transportation, packaging and assembly operations. However, in certain areas of application, such as indirect food contact, approvals for use need to be obtained from appropriate regulatory authorities.